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by

John M.C. Plane, Rod G. Zika, Richard G. Zepp*
and Lawrence A. Burns*

Rosenstiel School of Marine and Atmospheric Sciences
University of Miami
Miami, FL 33149
*Environmental Research Laboratory
U.S. Environmental Protection Agency
Athens, GA 30613

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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16. ABSTRACT

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Photochemical Modeling Applied to Natural Waters

John M.C. Plane[1], Rod G. Zika[1], Richard G. Zepp[2] and Lawrence A. Burns[2]

[1]University of Miami, Rosenstiel School of Marine and Atmospheric Sciences, Division of Marine and Atmospheric Chemistry, Miami, Florida 33149-1098

[2]U.S. Environmental Protection Agency, Environmental Research Laboratory, College Station Road, Athens, Georgia 30613

In this presentation an attempt is made to examine the application of modeling photochemical processes in natural water systems. For many photochemical reactions occurring in natural waters a simple photochemical model describing reaction rate as a function of intensity, radiation attenuation, reactant absorptivity and quantum yield is insufficient. Other factors governing the species distribution must be considered. These factors are divided into processes that cause production, decay, and mixing and transport. Three different photochemically active compounds are used as examples to illustrate how these various factors affect their distribution. Hydrogen peroxide is used as an example of a compound which is produced in situ, while trifluralin and pentachloro-phenol are compounds that have very different absorption spectra and are introduced from external sources. The photochemically mediated distribution of these example compounds is evaluated by taking into consideration the effects of light attenuation, equilibrium partitioning of the compound into nonaqueous phases (e.g. sediments), and physical mixing in the water column.

Many chemicals found in natural waters are photosensitive to sunlight. For instance, some trace organic species, of either terrestrial or in situ biological origin, photoreact to form reactive transients such as hydroxyl radicals, H_2O_2, O_2^-, or singlet oxygen. These products in turn typically exhibit further chemistry (1). Moreover, some transition metal complexes and inorganic species such as NO_2^- and NO_3^- can be photolyzed directly

by sunlight, changing their oxidation state and producing reactive products that are involved in further reactions (1).

The ability to model the chemistry of photoreactive species in natural waters is of great interest for four reasons. First, environmental photochemical modeling is necessary to extrapolate laboratory results to natural water systems. Modeling can be used to test hypotheses concerning the kinetics and mechanisms of photoreactions in the environment and to examine the contribution of competing processes that alter or form a chemical. Second, many photoreactive species are coupled to biological cycles; some are produced by organisms, while others may exert effects on them. In particular, knowledge of the effects of light on speciation of toxic organic chemicals or heavy metals can be of special importance. Third, recent research in the chemistry of the troposphere has shown that the oceans are probably an important source of several trace species found in the atmosphere. Because most biological and photochemical processes exhibit diel variations, there may be substantial corresponding variations in the air-sea exchange of photochemically and photobiologically supplied, and reactive gases. Current air-sea exchange rate calculations, however, generally do not take diel light variations into account. Gases for which natural waters are a source, such as COS, CH_3I, CH_3SCH_3, H_2S and CO, should vary dielly because their surface concentrations should be responsive to light intensity and to mixed turbulent dilution. Finally, photochemical modelling in conjunction with measurements of spatiotemporal distributions of transient photoproducts can be applied to estimate the age, origin, and mixing rates of water masses. This use of photochemically derived products to complement other tracer studies is a potentially powerful tool because the products of light-initiated reactions are often unique, are only generated in the illuminated upper layers of deep water bodies, and because the photoreaction rates can be described through standard chemical kinetic treatments.

In this chapter, we discuss some of the chemical, physical, and biological processes that are often significant in governing the distribution of photochemical reactants and transients in a water column. We are not concerned here with questions of horizontal transport, and our discussions are restricted to one-dimensional, mixed-layer, photochemical models. Examples of such models are presented where appropriate. Our discussion of the factors governing the distribution of chemical species in natural waters is divided into five parts--*in situ* photochemical formation, external sources, *in situ* photochemical decomposition, external loss, and turbulent mixing and transport. An attempt also will be made to indicate where laboratory measurements can be used as input into these models.

Factors Governing Species Distribution

In situ formation. The chemical and biological processes generating a chemical species (T) in natural surface waters may be symbolically expressed by the rate equation

$$d[T]/dt = Rf_l + Rf_d + Rf_b \quad (1)$$

where Rf_l is the rate of photochemical reactions that form T, Rf_d is the rate of thermal reactions forming T, and Rf_b is the rate of biological reactions forming T. For some compounds, Rf_d or Rf_b are important terms and may dominate the formation of T. An example of this is CO_2, which has large biological sources and probably very small photochemical sources through reactions such as the decarboxylation of organic acids. For some cases such as H_2O_2, it is difficult to obtain any direct information about Rf_b and Rf_d. Generating a model in terms of exclusive photochemical formation of T, and comparing model predictions with observed profiles of T in a water column, can often point to the relative contribution of these different transient formation terms.

Rf_l is a function of the quantum yield for the photochemical formation process, as well as the rate of light absorption by the photoreactive species. The rate of light absorption depends upon a variety of factors including the absorptivities and concentrations of the photoreactive species, and light intensity. Light intensity in turn depends on latitude, season, time of day, and cloud cover (2). Also, light intensity decreases with increasing depth because of attenuation by scattering and absorption.

It is often possible to obtain some information from laboratory measurements on quantum yields for a particular process. An example is a recent study on the formation quantum yields of H_2O_2 in several different natural waters (3,4). These quantum yield versus wavelength plots for all of the waters studied are surprisingly similar with the rate of production of H_2O_2 being a linear function of sample absorbance at the irradiation wavelengths. Recent studies (5,6) indicate that photoreactions of organic precursors, which are largely responsible for light attenuation in natural waters, make an important contribution to the production of H_2O_2 in seawater. The organic precursors are mixtures with poorly characterized chromophores, so it is not possible to define primary quantum yields for H_2O_2 photoproduction from the individual reactive species. The approach followed by Zika et al. (4) involved defining an apparent monochromatic quantum yield, C_λ, for the overall production process as the number of moles of H_2O_2 produced per Einstein of photons absorbed at wavelength λ. The monochromatic accumulation rate is then the rate of photons absorbed per unit volume of water, multiplied by C_λ. The quantity C_λ can be measured over the range of solar wavelengths in samples of seawater in the laboratory.

A depth profile of the differential spectral intensity of sunlight can either be measured using a multiple bandwidth underwater light detector and input directly into a photochemical model, or be calculated using a suitable light attenuation model. For example, the model of Zepp and Cline (2) calculated the attenuation of light in the water column due to absorption and scattering. The absorbance of the particular body of water of interest must be specified from observation. The model then specifies solar fluxes at sea level as a function of time of day, total ozone column density, latitude, and season, partially based on analysis of climatological data. This type of model can then be

adapted [e.g., see Zika et al., (4)] to calculate the rate of photons absorbed at a selected depth.

Finally, the monochromatic accumulation rate is integrated over the solar spectrum to obtain the total accumulation rate. The results of this procedure are illustrated in Figure 1, which shows the variation with depth of the photochemical rate of production of H_2O_2 at midday at 40°N for summer and winter in a freshwater sample. A rapid decrease of the rate with depth is apparent, particularly in this dark colored freshwater sample which attenuates most of the near-ultraviolet radiation in the upper 20 cm. Figure 2 shows how the calculated rate of photochemical production varies with time of day and extent of cloud cover at a chosen latitude and season.

External Addition of a Chemical Species

Two other source terms need to be considered. First, there is the possibility of dry or wet deposition of a chemical species to the water surface from the atmosphere. The rate of dry deposition depends on the concentration of the species in the gas phase, the concentration in surface water, the Henry's Law constant, and the reactivity of the species with seawater constituents, as well as the wind speed and the aerosol in the air adjacent to the water surface. The rate of wet deposition depends on the concentration of the species in the precipitation and the frequency and duration of precipitation events. Little information is currently available about these processes, although there is some evidence that a rainstorm can inject significant quantities of H_2O_2 into the upper meter of the water column. This effect is usually short-lived, however, due to rapid mixing (4).

Second, many natural and anthropogenic chemical species are injected into natural waters from terrestrial run-off or other environmental events.

In Situ Decomposition of a Chemical Species

The decomposition of a chemical species within the water column may be described by:

$$-d[T]/dt = Rd_d + Rd_{li} + Rd_{ld} + Rd_b \qquad (2)$$

where Rd_d represents rates of thermal reactions removing T, Rd_{li} and Rd_{ld} describe the rate of removal of T as a result of indirect and direct photochemical reactions and Rd_b represents the biological removal rate. Rd_d depends on factors such as the ionic strength, the composition and temperature of the water, and the concentrations of T and the materials with which it reacts.

Sufficient information for predictive estimates of rates of thermal and biological decay often are not available. Empirical rates determined by storing samples in the dark for periods of time can be used, but this procedure is prone to errors such as wall effects (7). The rate of indirect photochemical removal, Rd_{li}, is expected to be dependent on the same factors as Rd_d as well as the intensity of solar radiation in the water column. This solar

intensity determines the steady-state concentration of the species with which T reacts.

The rate of direct photochemical removal is dependent on the extinction coefficient and the quantum yield for the primary process. As an example of this process, consider the case of two compounds with very different absorption spectra illustrated in Figure 3. The effect of their rather different extinction coefficients on the rate of direct photochemical decomposition is demonstrated in Figure 4. These plots show the depth dependence of the decay constants in two water bodies with different light transmission characteristics. In the more opaque, moderately productive water, the rate coefficients decrease markedly with depth. In general, Rd_{ld} depends on the same factors as the rate of photochemical production, R_{fl}.

External Removal of a Chemical Species

Two types of physical loss processes should be considered in the external removal of a chemical species. First, the species of interest may be lost to the atmosphere through water-air exchange. This process depends on the Henry's Law constant for the chemical species, as well as the atmospheric concentration and the structure of the surface microlayers (8). Wind stress and turbulence of the water body surface have a pronounced effect, especially for surface-active materials for which bubble scavenging and surface film ejection as aerosol takes place. Transfer rates at the air-water interface are complex problems in themselves and are not dealt with in this Chapter.

The second important process to consider is physical loss of a transient by partitioning into sediments on the bottom or suspended particles in the water column. The potential significance of this loss term is demonstrated in Figure 5, a plot of the log of the partition coefficients between octanol and water (log P) for almost 20,000 industrial compounds. The narrow distribution of these coefficients is striking, the more so in the context of Figure 6.

Figure 6 illustrates pseudo-first-order system halflives, estimated by the Exams model (9), for photolysis of a series of generic organic substrates with differing K_{ow}'s ($P = K_{ow}$) and sediment/water partition coefficients, (K_p) but with the same photolysis rate constants in the water column of a freshwater pond. As the partition coefficients increase, the fraction of substrate in the illuminated water column, and thus the system halflife, decreases due to increased sorption into bottom sediments. It is noteworthy that this simulation, when compared with Figure 5, indicates that sorption into bottom sediments has little or no effect on the total rate of photochemical loss for a preponderance of industrial chemicals.

Turbulent Mixing Within and Below the Photic Zone

Any model of photochemistry in natural waters must take into account the effect of turbulent mixing on the concentrations of transient species and their diel and seasonal variations. For the oceans, the part of the water column of particular interest is the

upper 100 m. Photochemistry largely takes part in about the first 30 m (the photic zone), although this depth depends somewhat on the light transmission characteristics of the water.

Turbulent mixing near the surface is in many cases dominated by surface wind stress. Heat transport may also lead to vertical mixing. These mixing processes result in an homogeneous layer below the surface known as the mixed layer, the depth of which is largely a function of wind-stirring. This layer generally varies between 20 and 40 m over much of the ocean. The situation in lakes is similar except that the mixed layer is usually much shallower.

The aim of a turbulent mixing model is to assess the importance of mixing within the photic zone, and the way in which turbulence can mix water containing species that have either been photochemically produced or depleted, from the photic zone down to depths below the mixed layer. As indicated in the introduction, the aim of this Chapter is not to discuss the consequences of horizontal transport. For the oceans, such considerations are usually not necessary bearing in mind the homogeneity that is typically at a scale of several hundred kilometers, the velocity of horizontal transport, and the lifetimes of many photochemical species of a few hours to a few days (1).

When setting up a study, an investigator has several types of one-dimensional mixing layer models from which to choose. These models are distinguished by the ways in which they attempt to solve the one-dimensional conservation equations of momentum, heat, and salinity that describe the system. For instance, the turbulence closure model of Mellor and Durbin (10) has been used to model the photochemistry of H_2O_2 in the ocean (4). The results of this work will be used in the discussions below. This model uses second-order closure assumptions to reduce the conservation equations to two equations -- one for the mean specific turbulence kinetic energy and one for the vertical transport of specific horizontal momentum. This model has been criticized for its tendency to underpredict the depth of the mixed layer and the size of the step change in the temperature profile at the bottom of the layer, when compared with measurements.

Another approach involves the usage of eddy coefficients and mixing lengths. This method treats all transport by analogy to molecular diffusion, assuming that the turbulent fluxes can be expressed by the gradient of the transported quantity multiplied by an appropriate eddy diffusion coefficient. A recent example of this type of model is the work of Denman and Gargett (11) on phytoplankton in the upper ocean. This model is used for calculations presented later in this Chapter. Finally, bulk, mixed-layer models are available which assume that the top layer of the ocean is mixed thoroughly and that the vertical distribution of temperature, salinity, and horizontal velocity within this mixed layer is, if not uniform, then at least very much smaller than the variations across the layer boundaries or the variations within the thermocline.

The assumption of a uniform mixed layer permits vertical integration of the conservation equations and yields expressions for the turbulent transports in terms of the mean quantities and the external inputs. The turbulence energy equation is used to

obtain an expression for the evolution of the layer depth which is needed for closure. Examples of models of this type are those of Niller (12) and Garwood (13). The predicted temperature profiles of these models have generally compared well with measurements (14). Detailed comparisons between these different types of one-dimensional models, however, are not the purpose of the present discussion, and the reader is referred to the referenced papers and the review by Niiler and Kraus (15).

Once a model has been selected, an additional conservation or continuity equation is required to describe the transient species of interest. The eddy coefficients that govern the transport of the transient have been taken to be the same as those for heat transport [see e.g., (4)]. Thus, the temporal development of the transient can be modeled along with the development and diurnal variation of the stability of the water column. In this manner, the effects of wind-stirring and surface heat flux as well as of photochemical processes on the vertical profile of a transient can be investigated.

A recent example of such a model is that describing the distribution of H_2O_2 in the upper layer of the ocean (4), using the Mellor and Durbin model (10). Before considering the effect of turbulent mixing on transient distribution, refer to Figure 7, which shows the calculated time-depth profiles for H_2O_2 during winter in the Gulf of Mexico over a 2-day period beginning with sunrise, assuming the effects of photochemical processes alone and a complete absence of turbulent mixing.

The rates of photochemical production that were input into the model are taken from laboratory quantum yield measurements, discussed earlier (see section "In situ formation"). These are incorporated into a light attenuation model that employs the extinction coefficient of light in water with the clarity of the Gulf of Mexico. The dark decay lifetime of H_2O_2 was chosen to be 4 days, and constant with depth. The dark decay lifetime varies from hours in coastal environments to over a week in oligotrophic waters, but 4 days is commonly observed for offshore surface water (7). It is clear from Figure 7 that, in the absence of any mixing processes, H_2O_2 builds up to high concentrations with little diel variation because the dark decay lifetime is much longer than one day. As expected, H_2O_2 is not produced at all below the photic zone. Measurements of H_2O_2 in the Gulf of Mexico (16), however, reveal much lower surface concentrations and significant concentrations down to about 70 m, and turbulent mixing has been invoked to account for these observations.

The turbulent mixing model was set up in this case with an initial temperature profile of neutral stratification between the surface and 80 m, and then allowed to vary according to surface wind stress and heat flux. The initial deviation of the currents from geostrophy was assumed to be zero. The surface heat flux was allowed to vary dielly in a sinusoidal manner with a small constant heat flux superimposed, simulating net heating in summer and cooling in winter.

Figure 8 shows the calculated time-depth section of H_2O_2 over a 2-day period. To emulate heat flux conditions typical of autumn/winter, a surface cooling was superimposed on the dielly

varying heat flux, which has a noon-time maximum of 10^{-4} Km s^{-1}. The model was integrated for 10 days prior to the 2 days that are shown. The wind stress was set at a value of 1 dyne cm^{-2}, which roughly corresponds to a 10-knot wind.

A comparison between Figures 7 and 8 shows the significant effect that turbulent mixing can have on the vertical profile of H_2O_2 in the water column. During the day, surface heating establishes a stable layer in the upper 20 m that tends to trap most of the H_2O_2 produced in the surface water. The peak surface concentrations occur about 2 hours before sunset rather than at noon, when the maximum solar flux occurs, because H_2O_2 continues to accumulate during the afternoon, even though the light flux is decreasing.

After sunset there is a gradual erosion of the surface thermocline brought about both by nocturnal cooling and wind-stirring, which continue throughout the night and establish a deepening neutrally stratified layer approaching 20 m in depth shortly before sunrise. Once there is continuity established between the near surface neutrally stratified layer and the preexisting neutrally stratified layer below 20 m, any additional surface cooling will allow rapid mixing of the water down to the next thermocline at 70 m.

The calculated time-depth section of the 1-hour changes in H_2O_2 due to combined photochemical and transport processes is shown in Figure 9. This illustrates more clearly that the intense mixing is confined to relativley brief periods from shortly before sunrise to midmorning at greater depth. The intense mixing to 70 m depth is due to surface cooling superimposed on the diurnally varying heat flux as the cool surface water breaks through the inversion established during the previous day.

The increase in H_2O_2 is confined to the surface stable layer during the day and becomes uniform within the upper 20 m during the night. Once the 20 m thermocline is broken, this layer is rapidly flushed. Essentially all of the H_2O_2 between 20 and 70 m is rapidly injected within a few hours around sunrise. The size of this effect, of course, depends upon the magnitude of surface cooling during the course of the night. By contrast, in the summer months when there is a net positive heating of the surface water, a thermocline develops that traps the H_2O_2 at the depth where it is produced in the photic zone, except for some wind-stirring near the surface. This is shown in Figure 10. Wind-stirring produces a mixed layer deeper than the photic zone (cf. Figures 7 and 10), and the concentrations in the mixed layer are significantly higher than in winter because of the increased rate of production during summer.

The effects of varying the wind stress on the water surface also should be considered. For the purpose of illustration, the EXAMS II computer model (9) using eddy diffusion coefficients provided by Denman and Gargett (11), is used to compare the photochemical destruction of pentachlorophenol and trifluralin in natural waters. As was described earlier in Figure 3, these compounds have very different absorption spectra in the range of solar wavelengths, and hence different rates of photochemical decay (see Figures 5 and 6).

The results of the model calculations are shown in Figure 11. In all cases, the depth profiles that would have resulted with complete rapid mixing of the entire water column is shown for comparison. A uniform vertical distribution of substrate was assumed as the initial condition. In Figure 11a, the vertical profiles of the two compounds are compared over a 12-hour period, under conditions of low wind stirring and in moderately productive natural water. Trifluralin absorbs light up to about 540 nm and shows significant photochemical removal down to depths of about 30 m. By contrast, pentachlorophenol is photolyzed rapidly only at depths less than 10 m. In Figure 11b, the same comparison is made, but under high wind conditions. For both compounds it is clear that their concentration profiles follow the wind-stirred mixing layer that develops after a few hours and produces a well-defined base at about 25 m. This will be the case if the wind-stirring is strong enough, when turbulent mixing will become faster than the rate of photochemical destruction and a fairly homogeneous profile will result within the mixed layer.

Figures 11c and 11d demonstrate the effect of increasing the rate of photochemical decomposition by repeating the model calculations in Figure 11a and 11b, but now for the case of the clearest natural water. In Figure 11c, which illustrates the results for low winds, trifluralin is almost completely removed after 12 hours as solar wavelengths now penetrate down to 40 m. Pentachlorophenol is now significantly removed near the surface, but the rate of removal below 30 m is still slow (on the time-scale of 12 hours). Figure 11d is the case of high wind stirring. The profile of pentachlorophenol shows strong mixing and homogeneity within the mixed layer and follows the base of the mixed layer at 25 m. By contrast, the profiles of trifluralin show only slight discontinuities due to mixing, the result of the increased photolysis rates in the clear water competing with the wind-driven turbulent mixing.

Conclusions

In this Chapter, we have discussed in some detail the factors affecting the concentration of a photochemical reactant or transient product in the water column. These factors have been divided into processes that cause production, decay, and mixing and transport. In any model of photochemistry in natural water, all of these processes may be coupled together and all must be considered. It certainly should be clear from the examples in the last section that turbulent mixing plays a substantial role in determining the profile of the reactant or transient product in and below the photic zone.

The coupling of photochemistry and physical mixing in a model is a challenging task for three reasons. First, the photochemical production and decomposition rates, as well as the dark decay rates of interest, are often poor estimates. This is both because of the lack of good laboratory kinetic measurements and because the light attenuation models into which such measurements are incorporated are subject to additional uncertainties. Second, the one-dimensional mixing models make certain assumptions and

approximations in order to solve the momentum and heat continuity equations (15). The lack of precision of these mixing models must be borne in mind. Third, there is the question of obtaining suitable field measurements of reactant or transient product profiles in order to validate the prediction of a model. As analytical techniques improve, profiles can certainly be measured with higher accuracies.

When making a comparison with a model, however, there is the important question of the history of the water column in the few hours or days before a profile is measured. For example, if a profile of a transient was measured during a period of light winds, the model would predict a shallow mixing layer with the transient trapped near the surface, whereas a period of high winds shortly before might have mixed the transient well below the photic zone. Therefore, the model in this case would appear to have underestimated the depth of the mixing layer, depending of course on the lifetime of the transient. One way to get around this problem is to initiate the model with a measured transient profile and then have the model work forward in real time being continuously updated with relevant data such as the wind speed, cloud cover and surface heat flux, and periodically compared with measured profiles.

In spite of the difficulties that are present in developing models for aquatic photochemistry, much progress has already been made. Given the importance of being able to predict the distribution and lifetimes of many transients in the upper oceans and in freshwater, it is to be expected that a great deal of research will be done in this area in the future.

Acknowledgments

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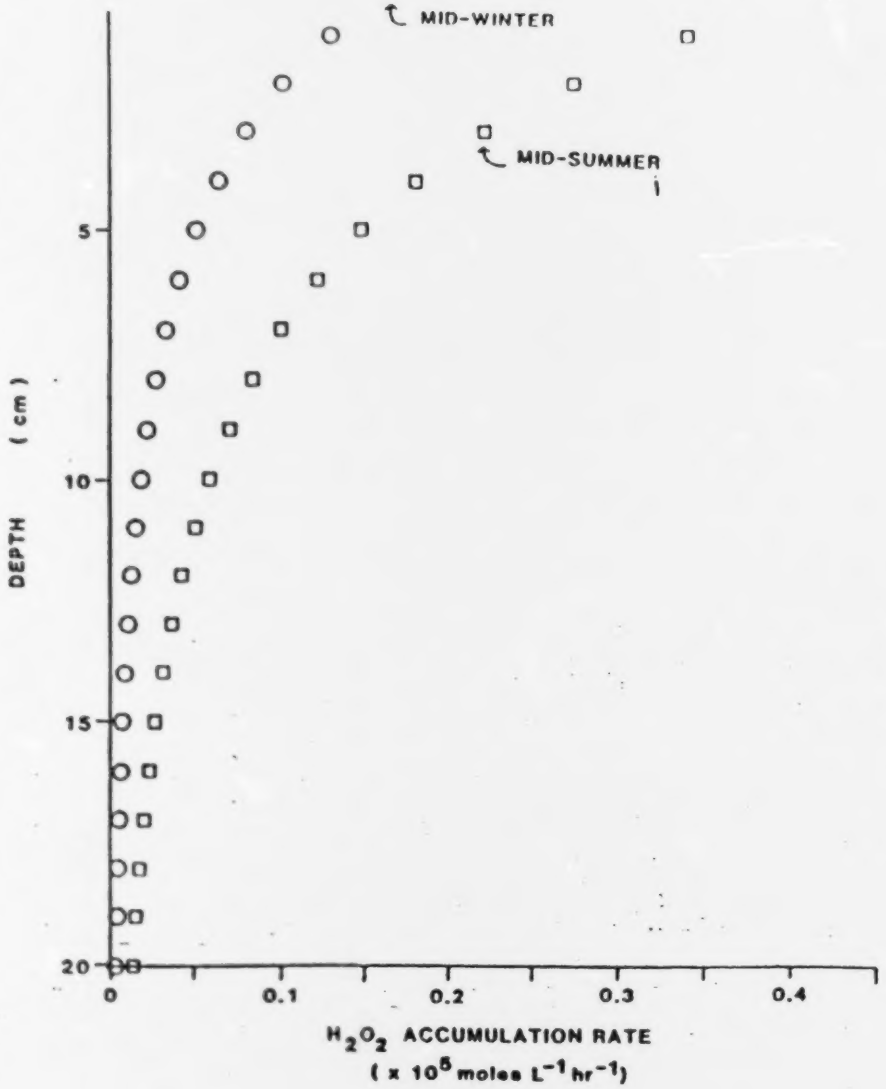

Figure 1. Photochemical model calculated accumulation rates of H_2O_2 versus depth for high organic material content freshwater sample from South Florida aquifer. Mid-day values at 40^0 latitude for two seasons are shown.

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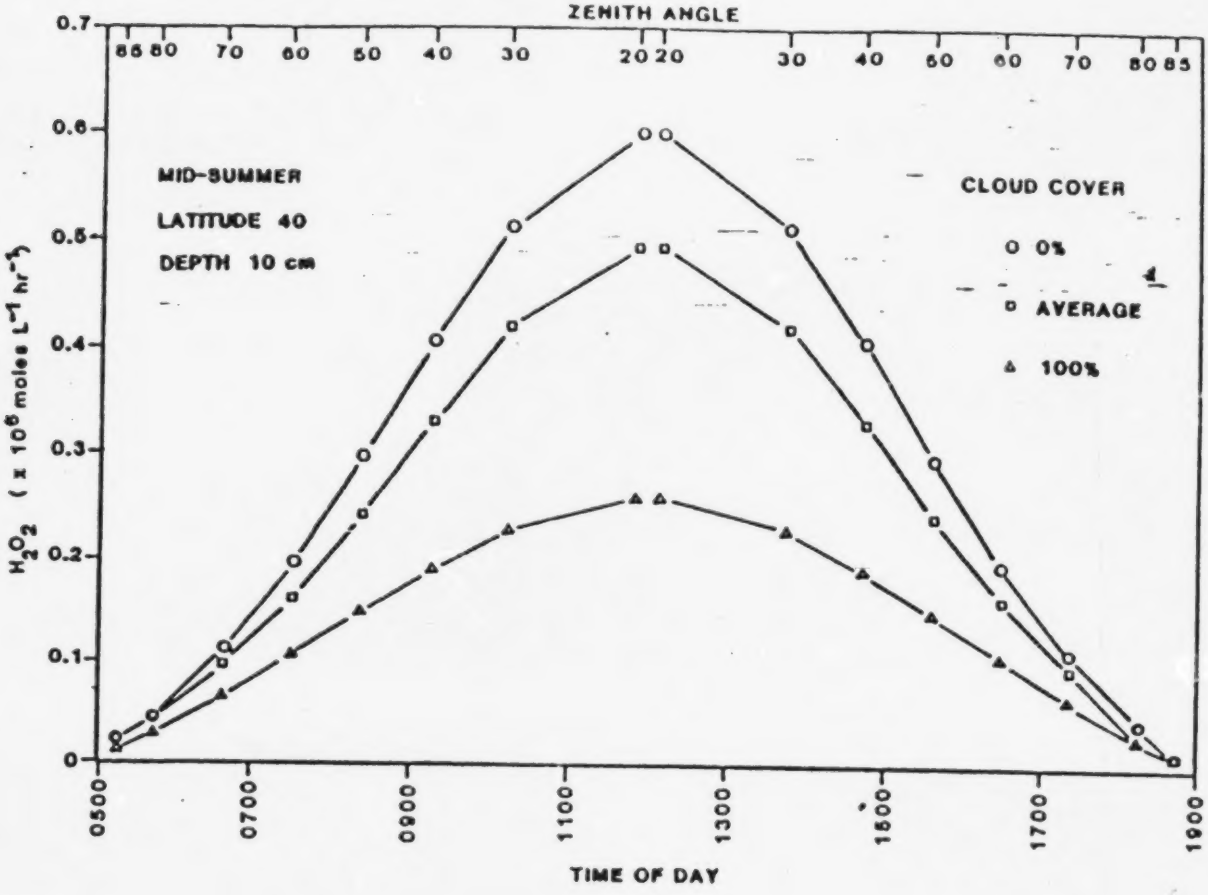

Figure 2. Photochemical model calculated H_2O_2 accumulation rates of H_2O_2 versus time of day in summer at 40° latitude and 10 cm depth for different extents of cloud cover. The water used was from a South Florida aquifer and contained a high level of organic material.

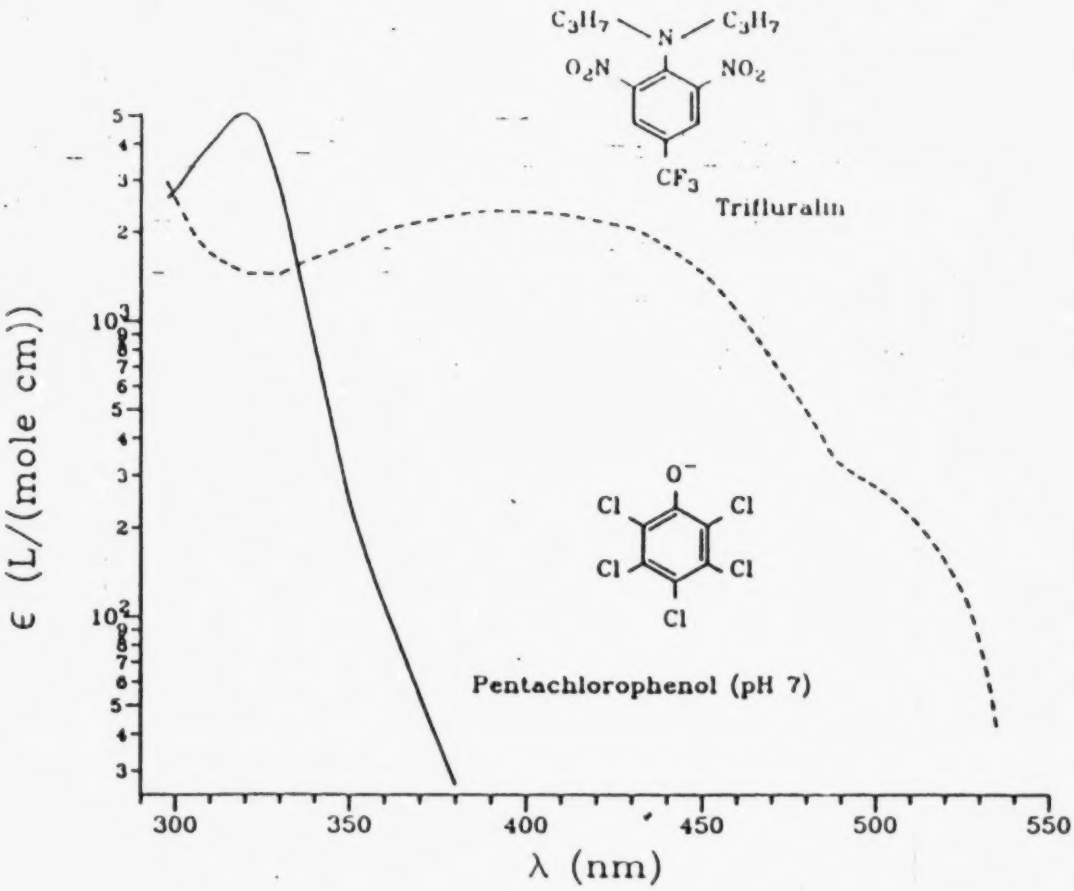

Figure 3. Electronic absorption spectra of pentachlorophenol and trifluralin in water.

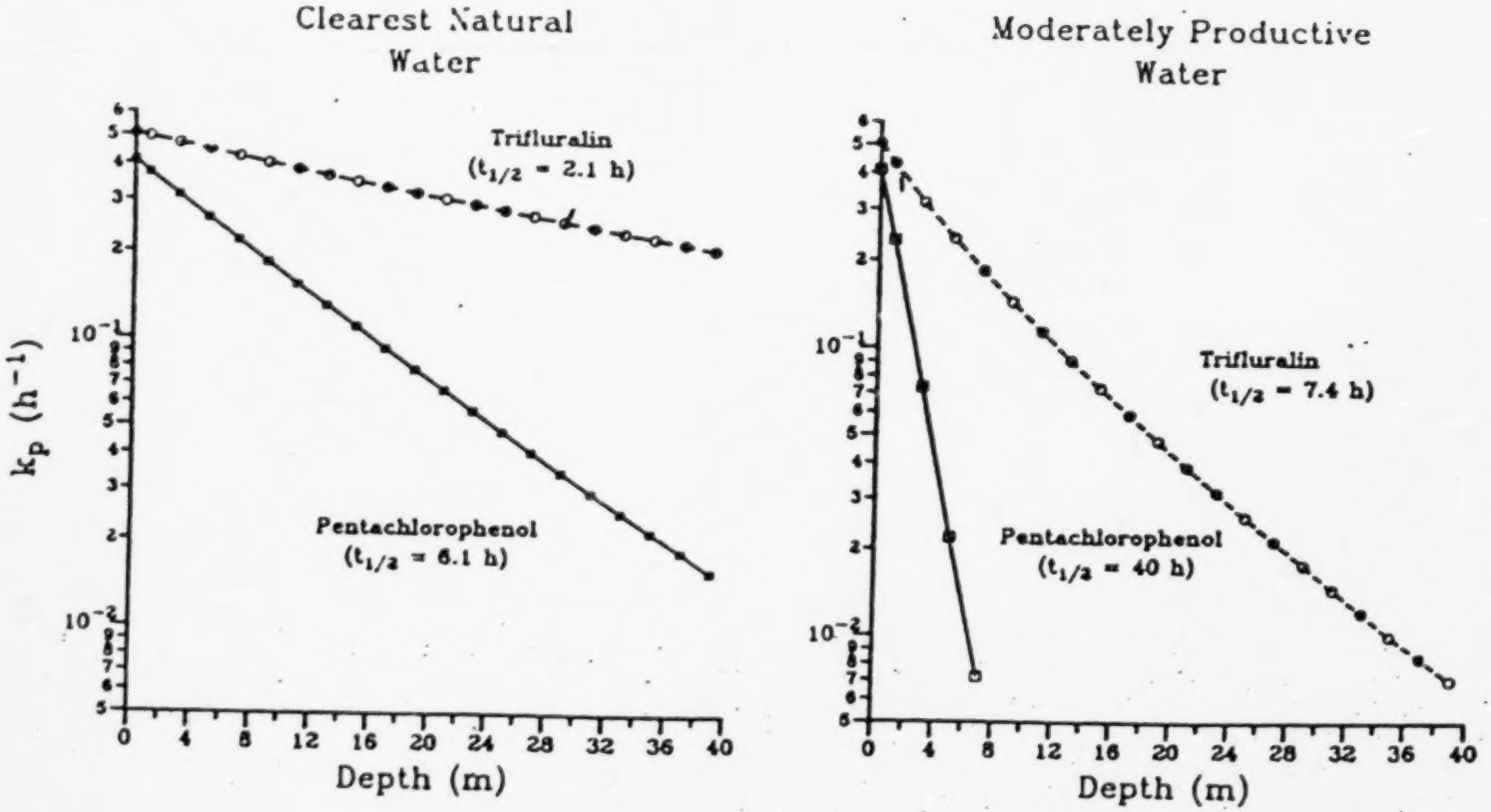

Figure 4. Computed depth dependence for the direct photolysis of trifluralin and pentachlorophenol in different water types (average rate constants parenthesized).

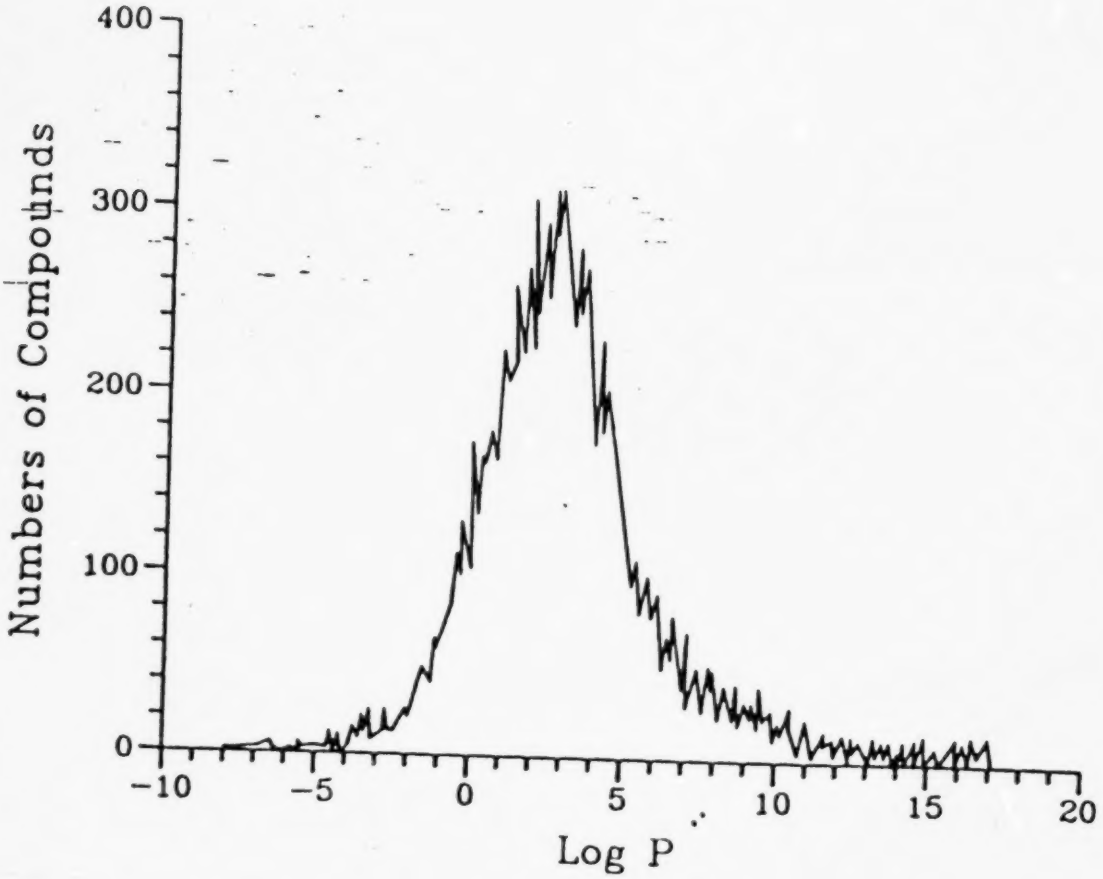

Figure 5. Distribution of octanol-water partition coefficients (P) computed for 19,965 industrial chemical (17)

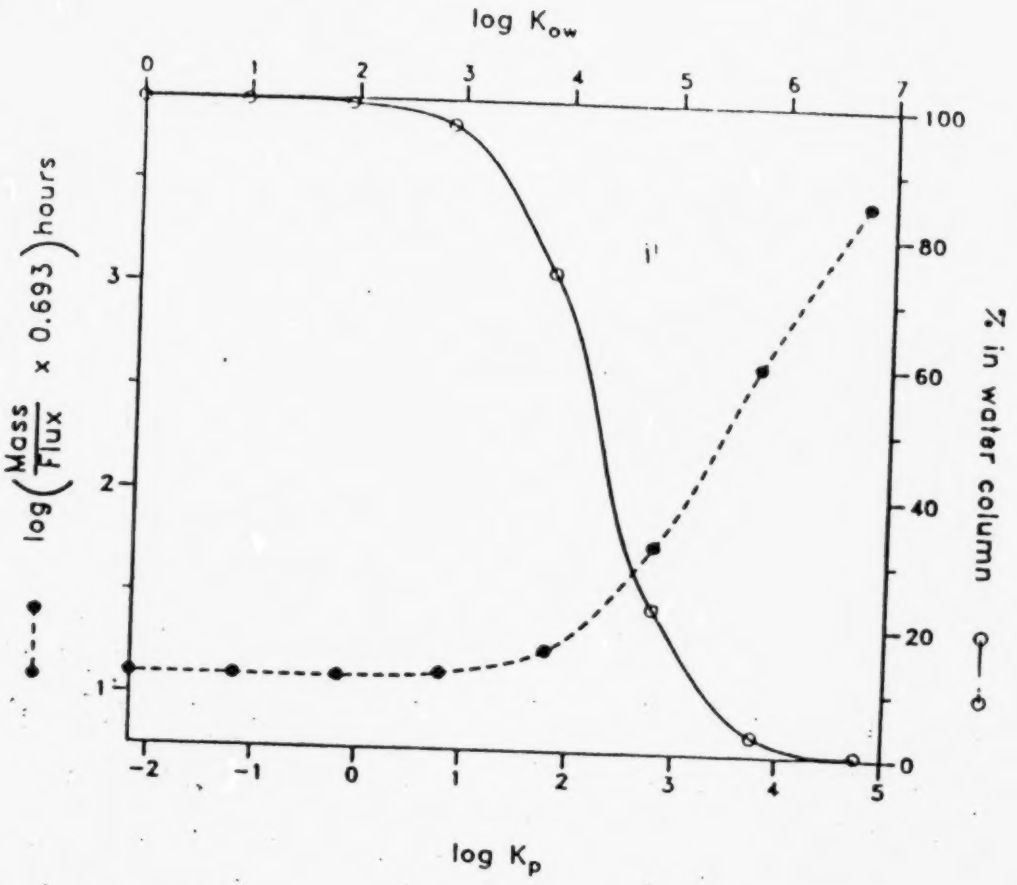

Figure 6. Computed effects of sorption to bottom sediments on the pseudo-first-order system halflives (log mass/flux) for a series of generic photoreactive substrates, each having the same photolysis rate but differing octanol-water partition coefficients (K_{ow}) and sorption partition coefficients (K_p).

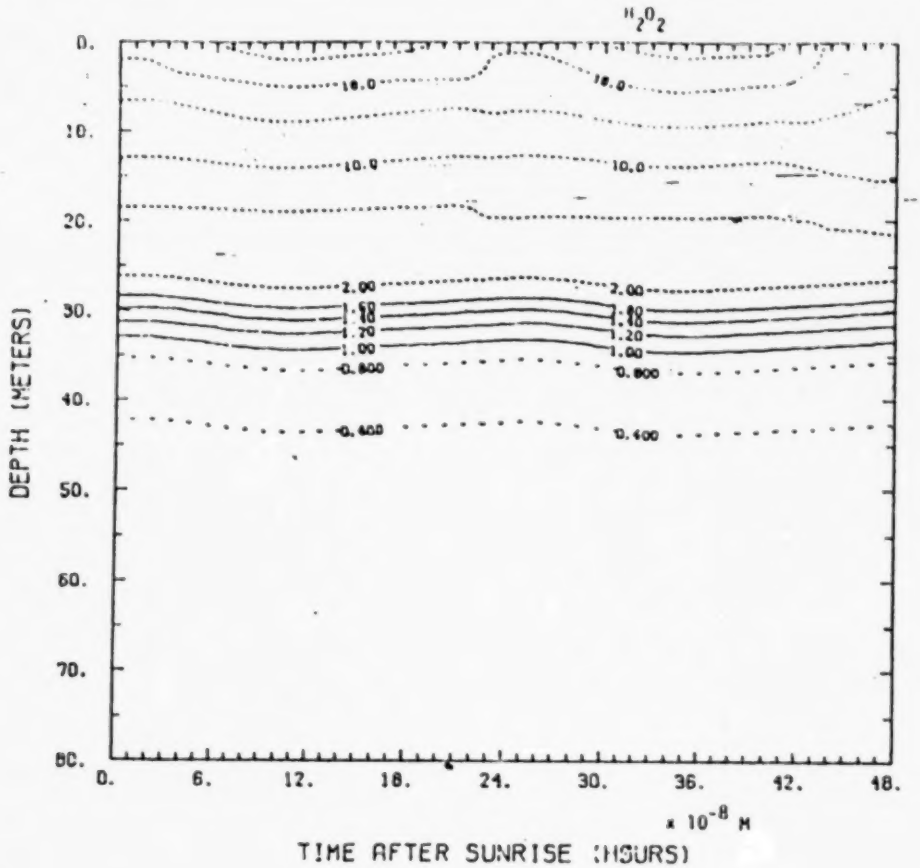

Figure 7. Calculated time-depth section of the H_2O_2 concentration due to photochemical production and destruction alone, over a two-day period beginning 0600 hrs local time. Conditions: mid-winter, latitude = 30°N, Gulf of Mexico.

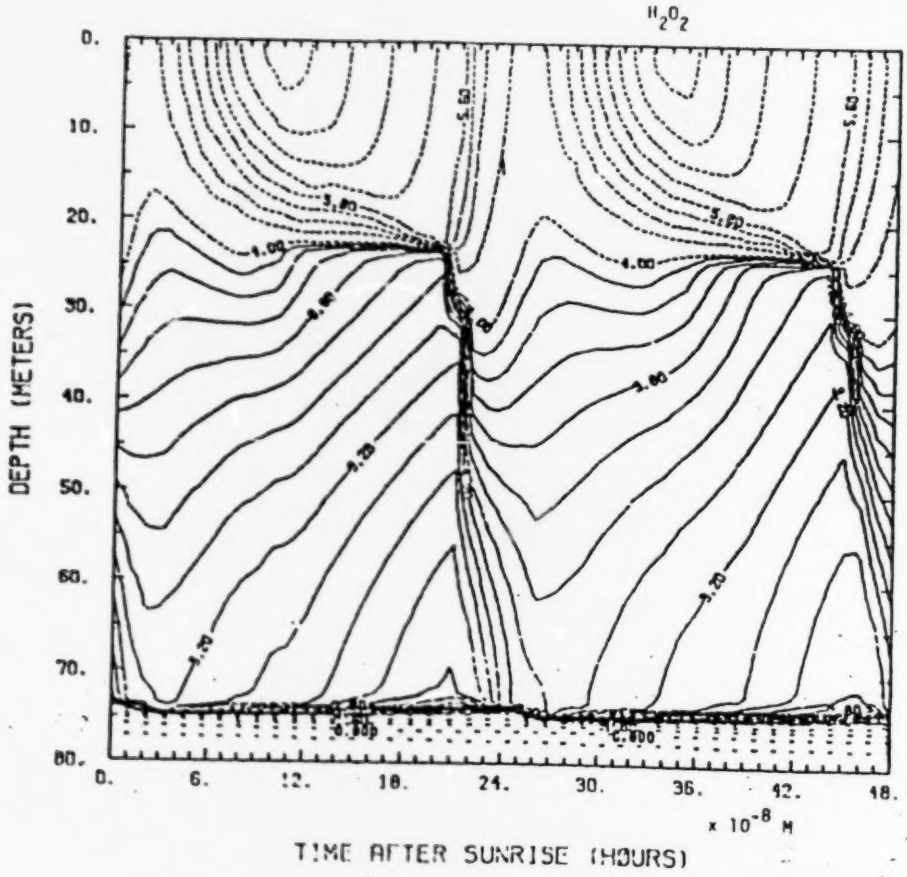

Figure 8. Calculated time-depth section of the H_2O_2 concentration, over a two-day period beginning 0600 hrs local time. Conditions: mid-winter, latitude = $30^{o}N$, Gulf of Mexico, wind stress = 1 dyne cm^{-2}, surface cooling = 10^{-1} Kms.

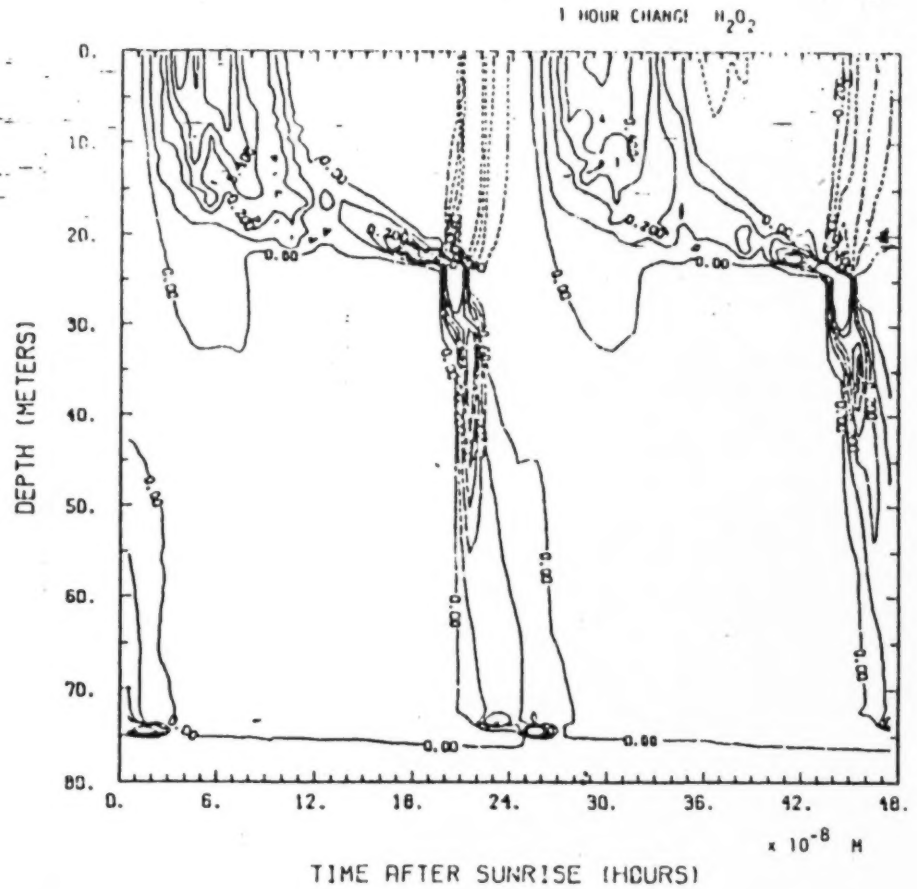

Figure 9. Calculated time-depth section of the one-hour changes in H_2O_2 over a two-day period beginning at 0600 hrs local time. Conditions: mid-winter, latitutde = 30^0 N, Gulf of Mexico, wind stress = 1 dyne cm^{-2}, surface cooling = 10^{-5} Kms^{-1}.

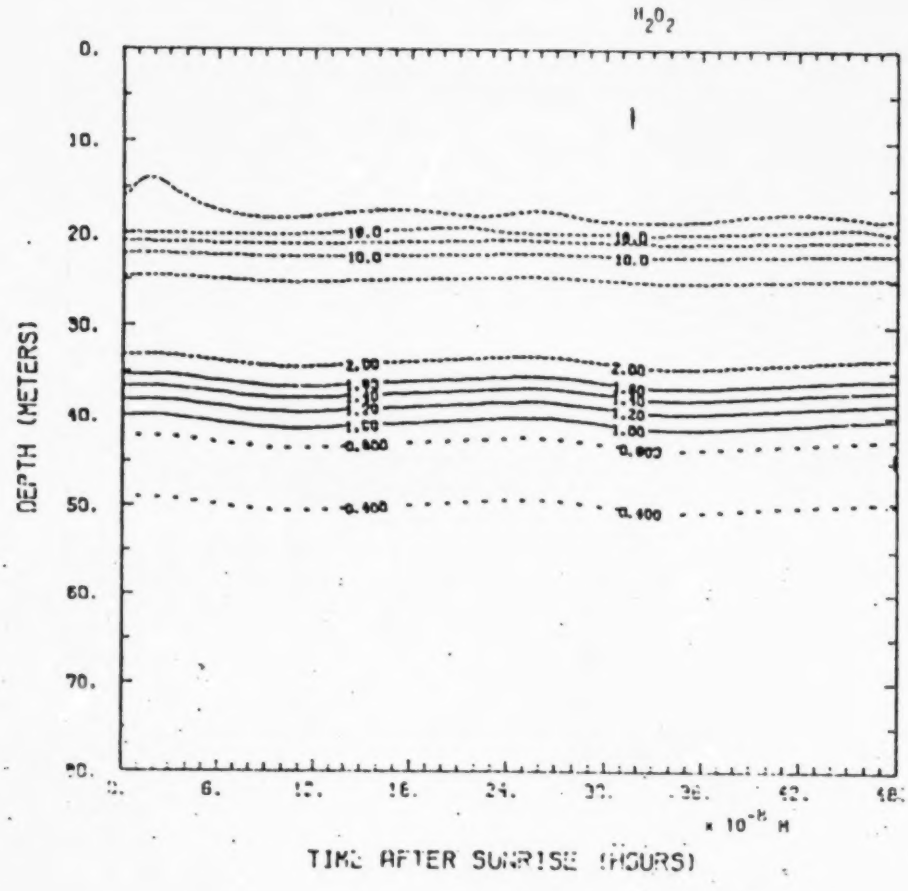

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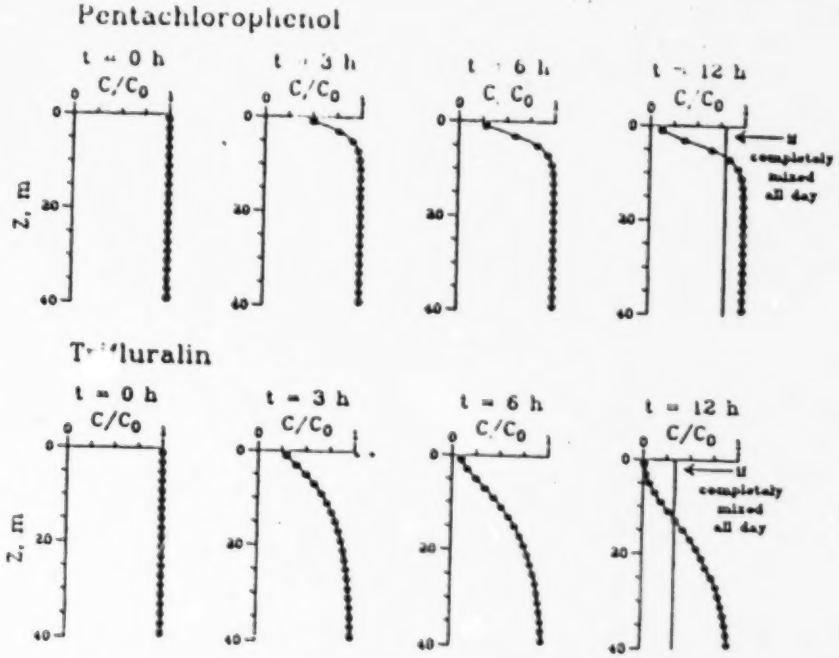
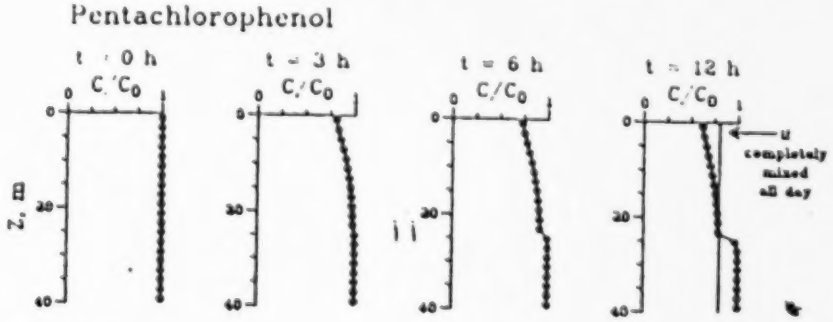
Figure 10. Calculated time-depth section of the H_2O_2 concentration, over a two-day period beginning 0600 hrs local time. Conditions: mid-summer, wind stress = 1 dyne cm^{-2}, surface heating = 10^{-5} Kms^{-1}.

Conditions: Moderately productive water, low winds (5 m s)



A

Conditions: Moderately productive water, high winds (15 m s)



B

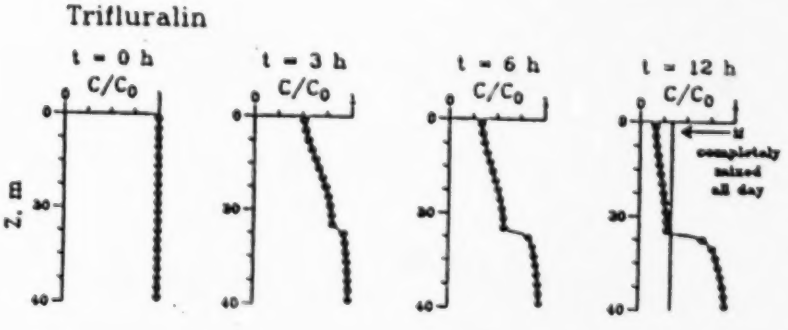
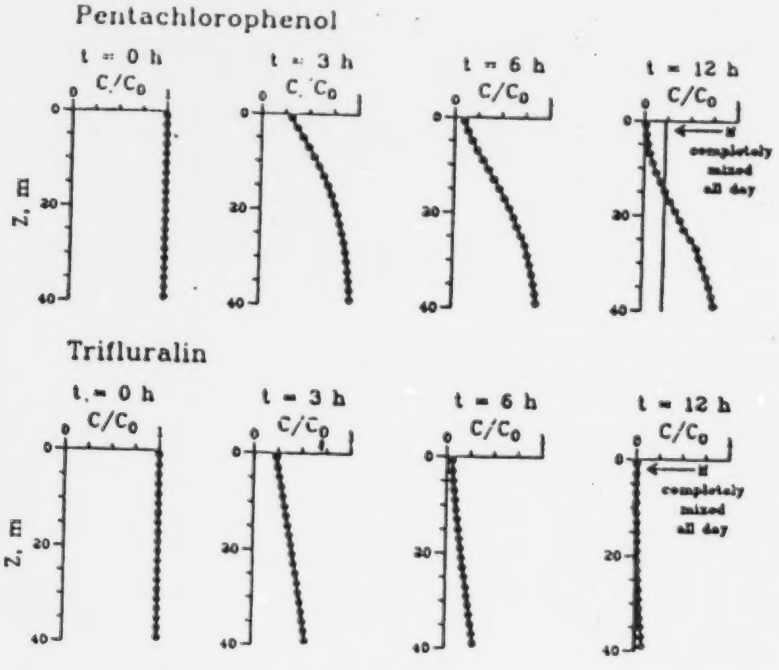


Figure 11. Vertical mixing effects on the computed concentration/depth profiles for pentachlorophenol and trifluralin (metalimnion at 25 meters): a) Moderately productive water, low winds, b) moderately productive water, high winds, c) clearest natural water, low winds, d) clearest natural water, high winds.

Conditions: Clearest natural water, low winds (5 m/s)

C



Conditions: Clearest natural water, high winds (15 m/s)

D